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CO_2 recycling using microalgae for the production of fuels

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Abstract CO_2 capture and recycle using microalgae was demonstrated at a coal-fired power plant (Duke Energy's East Bend Station, Kentucky). Using an in-house designed closed loop, vertical tube photobioreactor, *Scenedesmus acutus* was cultured using flue gas as the CO_2 source. Algae productivity of 39 g/(m^2 day) in June–July was achieved at significant scale (18,000 L), while average daily productivity slightly in excess of 10 g/(m^2 day) was demonstrated in the month of December. A protocol for low-cost algae harvesting and dewatering was developed, and the conversion of algal lipids—extracted from the harvested biomass—to diesel-range hydrocarbons via catalytic deoxygenation was demonstrated. Assuming an amortization period of 10 years, calculations suggest that the current cost of capturing and recycling CO_2 using this approach will fall close to \$1,600/ton CO_2, the main expense corresponding to the capital cost of the photobioreactor system and the associated installation cost. From this it follows that future cost reduction measures should focus on the design of a culturing system which is less expensive to build and install. In even the most optimistic scenario, the cost of algae-based CO_2 capture is unlikely to fall below \$225/ton, corresponding to a production cost of ~\$400/ton biomass. Hence, the value of the algal biomass produced will be critical in determining the overall economics of CO_2 capture and recycle.

Keywords Microalgae · Carbon dioxide · Flue gas · Capture · Techno-economic analysis · Biofuels

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Introduction

Despite concerns surrounding the contribution of fossil fuel combustion to global warming, the need for fossil fuels will remain significant for the foreseeable future. With direct replacement unlikely, strategies to reduce the emitted CO_2 are in high demand. The current array of options encompasses four main areas: (1) modifications to existing power plants to increase the efficiency of combustion, (2) improvements to the efficiency of energy use by consumers, (3) chemical carbon capture with subsequent sequestration, and (4) bio-mitigation with carbon recycling. All of these methods have promise, yet they are beset with significant technical and non-technical challenges. Alterations to the methods of use and production involve issues related to expensive plant modifications or changes to the behavioral patterns of consumers. Despite technological gains for CO_2 capture and sequestration, the costs associated with energy-intensive CO_2 concentration and compression are significant and anticipated to result in a parasitic power plant load on the order of 30–40 %. In addition, the uncertainty surrounding risk and liability issues related to long-term geologic sequestration is potentially strong enough to deter investment and adoption.

As is frequently stated, microalgae are the fastest growing photosynthetic organisms with growth rates and CO_2 bio-fixation potentials generally in excess of terrestrial plants [21]. Depending on growth conditions (light intensity, temperature, and physical nature of the environment), the levels of available CO_2, and the nutrient needs of the organism, a combination of carbohydrates, proteins, and lipids are produced. From these metabolites a range of fuel and chemical feedstocks/resources can be produced [4, 29]. It is this combination of growth rate and lipid productivity that has led to algae being touted as an ideal source of bio-derived oil [28].

The use of microalgae-based CO_2 mitigation suffers from two principal disadvantages: (1) in bio-mitigation, CO_2 is captured and subsequently recycled (effectively, the carbon is used twice); in other words, CO_2 is not permanently removed from the carbon cycle; and (2) a range of challenges exist which are primarily related to system complexity and scale-up issues that are driven more by economic constraints than technical issues. However, biological carbon capture and recycling has the potential to generate a revenue stream to offset, at least in part, the overall cost of implementation [12]. Indeed, the use of algae as a carbon dioxide bio-mitigation strategy and as a potential source of renewable fuels has long been a focus of research and development [2, 5, 7, 14, 16, 20]. A primary concern is that the cultivation strategy selected (typically a large shallow open pond) requires vast amounts of water and land. This is further complicated by the need to keep the algae cultivation system close to the carbon dioxide source, where a primary limiting factor becomes the suitability of the available land. To resolve this problem, most studies have inferred that the optimal approach would be to construct a fossil fuel power facility where land availability is not a problem for large-scale cultivation; however, this solution does not resolve the issue of carbon dioxide mitigation from existing fossil fuel energy production facilities, or, for that matter, other types of CO_2 point sources.

A few recent reports have attempted to address these challenges through the development of closed loop photobioreactors, which on an areal basis are typically more productive than open ponds [33]. Indeed, a study by Doucha et al. [10] employing flue gas from a natural gas fired boiler fed to a thin layer photobioreactor containing *Chlorella* sp. found that up to 50 % CO_2 removal could be attained. A study reported by Vunjak-Novakovic et al. [31] placed this figure as high as 82 % on sunny days for *Dunaliella* strains grown in an airlift reactor, with 50 % CO_2 removal on cloudy days. An older study by Laws and Berning [17] performed in Hawaii using the marine chlorophyte *Tetraselmis suecica* (grown in outdoor flumes) indicated that CO_2 emitted from an oil-fired electric plant could be successfully substituted for pure CO_2 for the cultivation of algae. More limited than the number of these studies are the commercially viable microalgae production processes that utilize flue gas from power plants. In fact, only Seambiotic in Israel has produced significant quantities of algae in this manner, using the flue gas from the Israel Electric Corporation's coal-fired Ashkelon power plant (Seambiotic [27]).

Against this background, we set out to determine the technical and economic feasibility of algae-based carbon capture in Kentucky. This required designing and demonstrating a process capable of utilizing flue gas through operation of a continuous microalgae culture, and evaluating the economics of CO_2 capture using this approach. This paper summarizes the results of our initial work, including the development and scale-up of component technologies, and demonstration of the integrated process at Duke Energy's East Bend Station, situated in northern Kentucky.

Experimental

Algae culturing

Scenedesmus acutus was obtained from the University of Texas Culture Collection (UTEX B72) and was used for all experiments. Cultures were grown in urea medium previously optimized for this *S.* strain (Crofcheck et al. [8]). Initial cultures were grown in 500 mL Erlenmeyer flasks under warm (Philips F32T8/TL741 Alto, 32 Watts) and cool white (Philips F32T8/TL735 Alto, 32 Watts) fluorescent lights [70 μmol/(m^2 s)] in a 16:8 h light:dark illumination period. Flasks were bubbled with 3 % CO_2 (from gas cylinders) and kept at room temperature (22 °C). The flask cultures were eventually transferred to 7.5 L airlift photobioreactors (PBRs). These airlifts also received a constant supply of 3 % CO_2, but were grown under natural light conditions in a greenhouse. A number of airlift PBRs were used to inoculate a 650 L Varicon BioFence PBR which, in turn, was used to seed a 1,000 L PBR. Both of these large greenhouse reactors were needed to produce enough algae to inoculate the East Bend Station PBR. The larger PBRs were constantly monitored by probes for pH (Hach DPD1R1), dO_2 (Hach 5740DOB), temperature, dCO_2 (Mettler Toledo InPro 5000i), and photosynthetically active radiation (PAR, Apogee Instruments SQ-215). The large greenhouse PBRs were fed CO_2 whenever the culture pH rose above a certain set point (usually pH 7.0). The East Bend Station PBR operated the same way using flue gas as its CO_2 source.

Culture growth was monitored by means of dry mass (g/L) (Crofcheck et al. [8]) and qualitative microscopy analyses. In addition, ultraviolet–visible spectrophotometry

(Thermo Scientific Evolution 60) was used to monitor the density of algal cultures, absorbance being measured at 680 nm. Typically, one 50 mL sample was taken daily from the PBRs for analysis. In addition, ion and urea concentrations in the cultures in the large PBRs were monitored on a regular basis by ion chromatography (IC) and high performance liquid chromatography (HPLC), respectively. The concentrations of urea and specific nutrient ions were tracked to determine the rate of nutrient consumption. Elemental analysis of harvested algal biomass was conducted using inductively coupled plasma-optical emission spectroscopy (ICP-OES).

Lipid extraction and purification

The algae used in all experiments were *S. acutus* (UTEX B72) autotrophically cultured at East Bend Station using a urea-based medium (Crofcheck et al. [8]). After harvesting and dewatering, the algae (10–15 % solids) were dried in an oven at 60 °C for 24 h. The oven-dried *S.* algae were ground up in a coffee grinder until the algae particles were reduced to a size of <1 mm. After grinding and before all extractions, the algae used in the extractions were heated to 100 °C for 20 min to remove residual water (moisture content <3 wt%). Extractions were performed according to the Bligh–Dyer method [3] with one modification, namely, a biomass to total solvent ratio of 10 g/180 g was used. After removal of solvent, the crude lipid was weighed, re-dissolved in $CHCl_3$ and filtered through a plug of K10 montmorillonite (Sigma-Aldrich) to remove the chlorophyll present (which remained strongly adsorbed on the clay). Solvent was then removed under vacuum to afford the purified lipid as a colorless waxy solid.

Lipid conversion to fatty acid methyl esters

Algal lipids were converted to the corresponding methyl esters using a two-step process of esterification (to convert free fatty acids) and transesterification (to convert triacylglycerides) (Canakci and Van Gerpen [6]). 1 g of extracted, purified algal lipids was mixed with 1.5 mL anhydrous methanol containing 2 % H_2SO_4 (wt/wt) and refluxed at 65 °C for 2 h. The reaction was then cooled in an ice bath and the contents were mixed with approximately 3 mL of a 1:1 (v/v) mixture of water:cyclohexane. The organic layer was extracted, dried over sodium sulfate and the cyclohexane was removed by a rotary evaporator. The remaining lipid was then reacted with methanol containing potassium methoxide (0.5 wt% of lipid feedstock). This mixture was refluxed at 65 °C for 30 min. The reaction contents were then cooled, mixed with a water:cyclohexane mixture and the organic layer was separated, dried over sodium sulfate and the cyclohexane was removed on a rotary evaporator. FAME analysis was performed using an HP6890 GC equipped with a J&W Scientific HP-88 capillary column (30 m × 250 μm × 0.2 μm). The inlet was set to 250 °C. The split ratio was 20:1 with a constant flow of 1 mL/min. The oven began at 50 °C and was ramped at 20 °C/min to 140 °C and held for 5 min prior to a second ramp of 3 °C/min to 240 °C. The detector was held at 300 °C. The GC was calibrated using a 37-component FAME GC standard (Sigma-Aldrich). Samples were diluted 1,000:1 in cyclohexane and toluene was used as an internal standard.

Lipid conversion to hydrocarbons

Lipid deoxygenation experiments were performed in a fixed bed stainless steel tubular reactor (1/2 in. o.d.) equipped with an HPLC pump. 0.5 g of Ni–Al LDH catalyst (particle size 150–300 μm) was first reduced under H_2 at 400 °C for 3 h. Details of the catalyst preparation and characterization have been reported elsewhere [25]. After reduction of the catalyst, the system was taken to the reaction temperature (300 °C) and pressurized with H_2 to 580 psi. A 1.33 wt% solution of the algal lipids dissolved in dodecane was introduced to the system at a rate of 0.1 mL/min along with a flow of H_2 (50 mL/min). Samples were collected from a liquid/gas separator placed downstream from the catalyst bed. The liquid feed and reaction products were analyzed using an Agilent 7890A GC equipped with an Agilent J&W DB-5HT column (30 m × 250 μm × 0.1 μm), an Agilent Multimode inlet, a deactivated open ended helix liner and a flame ionization detector (FID). Data acquired using the GC-FID were processed using SimDis Expert 9 software purchased from Separation Systems, Inc. The dodecane solvent was subtracted and/or quenched from the chromatogram prior to processing the chromatographic data. Further details can be found in [25].

Results and discussion

Photobioreactor development

The cultivation of an autotrophic organism requires the provision of a controlled growth environment, which involves exposure of the organism to appropriate levels of sunlight, CO_2, and nutrients [30]. The mass cultivation of algae can be realized in either an open culture system (pond), or a closed loop system (photobioreactor). The selection of an open or closed culture system revolves around a number of system parameters: (1) the microalgae to be cultured, (2) the anticipated carbon source, (3) the accessibility to required resources, and (4) the cost of construction, operation, and maintenance of the culture

system. Based upon simple mass balance calculations, an algae unit size to reduce the CO_2 output of a power plant would need to be of an enormous scale. Photobioreactors (PBRs) were chosen as the cultivation method in this study on the basis of their higher areal productivities [33] and limited water loss [30] due to evaporation. A number of prototype reactors of different configurations were first constructed in an effort to incorporate the lessons learned into larger scale reactors. Specifically, variations in construction materials, tube orientation and spacing, as well as flow patterns, were examined. The most important factor in designing photobioreactors is to allow exposure of the algal culture to sunlight to drive photosynthesis. Given that a vertical system typically enables a higher surface to footprint ratio than other configurations, a design based on a tubular photobioreactor was selected, oriented vertically, and constructed from low-cost, off-the-shelf parts.

The hydrodynamics of the reactor is another area of specific concern. Having a good understanding of the flow characteristics of the PBR is an important step toward enabling process control. Having a well-mixed system, with even flow and limited dead zones, ensures that measurements taken at a centralized point are descriptive of the entire system. In addition, any stagnant areas or zones with lower flow (with the potential to collect biomass) should be limited. If the biomass remains trapped in the reactor it can degrade and release compounds that affect culture health. Moreover, poor mixing can lead to anaerobic conditions which favor microbial denitrification, resulting in N_2O emissions [11, 15]. Given that N_2O is a potent greenhouse gas (GHG), this negatively affects the GHG balance of the system.

Different methods for circulating the algal culture and keeping it well mixed were, therefore, evaluated before developing a series flow, serpentine-style PBR (Fig. 1). This style of reactor most closely resembles a plug flow reactor, and is constructed by connecting multiple tubes in series to provide the algae access to the solar radiation needed to drive growth. Initial concerns over oxygen accumulation and low carbon dioxide levels were set aside due to the relatively low kinetic rate of photosynthesis (Grima et al. [13]). In order for detrimental concentrations of dissolved O_2 to accumulate, the liquid path, and thereby the residence time, would have to be extremely long. If care is taken in overall reactor design and operation, this issue can be resolved.

Historically, one of the main challenges in algae cultivation is CO_2 limitation. Carbon constitutes almost 50 % by weight of the elemental composition of algal biomass, with CO_2 representing the most significant nutrient requirement. One of the inherent benefits of working with coal flue gas is the high percentage of CO_2 in the gas (10–15 %) as compared to atmospheric conditions (0.04 %). Introducing CO_2-rich gas to the system can often be energy intensive, as is the case in systems requiring gas compression and bubbling. To minimize the costs associated with CO_2 entrainment, while maximizing mass transfer, a liquid driven vacuum pump (i.e., venturi or eductor) was employed in this study. An eductor uses the Bernoulli principle to entrain gas in a driven liquid flow. The extremely turbulent nature of the biphasic flow encourages good mixing and mass transfer, thereby facilitating CO_2 dissolution in the growth medium.

Photobioreactor operating strategy

Daily productivity rates of algal cultures are dependent on multiple factors, including the nature of the organism being cultured, nutrient concentrations, the concentration of dissolved carbon, temperature, light intensity (i.e., photosynthetically active radiation, PAR), and pH. In this study

Fig. 1 CAD image showing PBR design and photograph of the PBR installed in a greenhouse

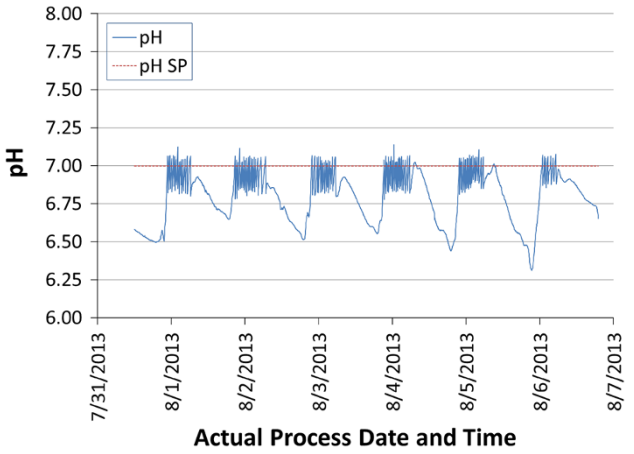

Fig. 2 Photobioreactor pH control. pH SP refers to the pH set point

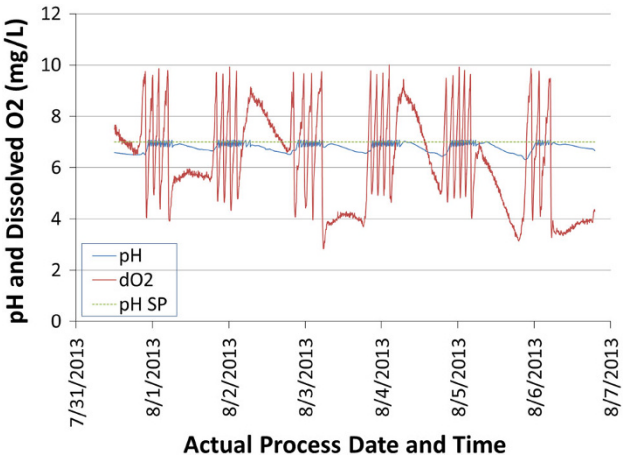

Fig. 3 O_2 production and system pH. The oscillations of the dO_2 signal are due to automated sparging of the culture with N_2 to maintain the dO_2 concentration below the set point value of 10 mg/L

S. acutus was cultured, a prior screening study having shown it to be appropriate for CO_2 capture based on its robust growth, tolerance to a wide range of pH values (Crofcheck et al. [9]), as well as ease of harvesting. Combustion flue gases can be a rich source of CO_2 for algae cultivation; however, the addition of excess flue gas must be avoided as this can result in over-acidification of the culture medium. This can be achieved by feeding CO_2 (as flue gas) on demand based upon the pH of the system. As algae grow, consuming CO_2, the pH of the solution is increased. The introduction of a CO_2-rich gas increases the concentration of carbonic acid and other dissolved carbon species, thereby lowering the pH. This approach maintains the system pH within an optimum pH range for algal growth while providing enough CO_2 to sustain growth. This is particularly important if other acidic flue gas components such as SOx and NOx are present. The dissolution of SOx in particular, which forms H_2SO_3/H_2SO_4, can result in over-acidification of the culture medium, thereby inhibiting growth (Crofcheck et al. [9]). For this reason, it is important that SOx is not added to the cultivation system faster than its dissolution products can be utilized by the algae.

Figure 2 illustrates the pH control method used to regulate CO_2 flow to the reactor during 6 days of algal cultivation in a 650 L PBR. The horizontal line indicates the pH set point of the reactor, while the trace shows the measured pH of the system. This graph also captures the occurrence of respiration, which produces CO_2, thereby lowering the pH during the night hours.

Appropriate reactor design can eliminate the buildup of O_2 in the photoactive portion of the reactor, but dissolved O_2 accumulation can still occur in a closed system over time. Elevated levels of dissolved O_2 can inhibit photosynthesis so it is important to have a method to remove excess O_2 from the system (Weissman et al. [32]). One method is to periodically sparge the main process tank with an oxygen-lean gas (such as post-combustion flue gas or nitrogen) which will remove dissolved O_2 preferentially over dissolved CO_2. Figure 3 shows the response of a PBR with N_2 sparging to remove excessive O_2 concentrations (i.e., >100 % atmospheric saturation or ~9 ppm). As anticipated, a high frequency of pH oscillation (corresponding to strong CO_2 consumption) is paired with a strong response in dissolved O_2. The effects of respiration on the pH and dissolved O_2 concentration during the night are also illustrated.

Another important variable that must be controlled is the culture density of the reactor. As a culture increases its number of cells, the increased chlorophyll concentration of the culture attenuates light much more quickly, starving some cells of required levels of solar radiation. Regular harvesting and dilution of the culture are, therefore, required to maintain a stable system capable of operating for an extended period of time.

Demonstration facility

Field testing of the system described above was conducted at Duke Power's East Bend Station (650 MW) located in Boone County, Kentucky. This single unit plant burns high sulfur coal as the fuel source and utilizes a wet limestone scrubber for SOx control and selective catalytic reduction (SCR) with ammonia injection for NOx control. Flue gas used for algae growth studies was obtained after the scrubber and SCR treatments with typical composition summarized in Table 1.

The site layout consisted of a PBR tube array located on an embankment situated approximately 7.5 m above a lower level where the 19,000 L feed tank, 5,700 L harvest tank and system control enclosure were located. The PBR assembly was constructed on a concrete pad poured above

Table 1 East Bend flue gas analysis (3/1/11–3/1/12)

	CO_2 (%)	NOx (ppm)	SO_2 (ppm)
Average:	8.9	53.4	28.0
Minimum:	7.2	14.5	6.5
Maximum:	9.6	97.2	84.3

Table 2 Analysis of source water at East Bend Station (average value of duplicate measurements ± standard deviation)

Analyte	Concentration, ppm
Chloride	3.79 ± 0.01
Nitrate–N	3.89 ± 1.17
Sulfate	25.15 ± 0.21
Phosphorus, total	<0.04
Calcium	89.45 ± 2.90
Magnesium	28.10 ± 0
Hardness by calculation	335.5 ± 12
Potassium	1.17 ± 0
Sodium	4.11 ± 0.78

a gravel drainage bed lined with a geomembrane below a French drain to collect all surface run-off and potential tube leakages. The drain flowed down the 7.5 m embankment to another concrete pad poured to provide a stable foundation for the feed and harvest tanks.

Water used to fill the PBR was drawn from several wells located on the property; typical analyses are shown in Table 2. Before water was fed into the PBR, it was passed through a UV sterilizer to minimize potential contamination by any organisms that may be present in this otherwise untreated water.

The PBR was constructed of clear PET (polyethylene terephthalate) tubes (8.9 cm diameter × 244 cm high) connected by 7.5 cm diameter schedule 40 PVC (polyvinyl chloride) pipe. Reactor tubes were arranged in 10 parallel flow paths, each consisting of 51 tubes connected in a serpentine path extending linearly for 18.3 m (Fig. 4). Feed was introduced by a centrifugal pump via a manifold where flow velocity through each tube was maintained at 16 cm/s, providing a residence time of approximately 13 min in the photosynthetically active volume of the clear tubes for each pass through the PBR. At the end of the PBR, the flow from each parallel flow path was combined in a common manifold and returned to the feed tank. As the return volume flowed back to the top of the 19,000 L feed tank, flow was directed to fall through T-pipe fittings to create suction, which was used as a means to introduce flue gas into the system (see Fig. 5 for a schematic of the PBR system).

The suction end of the return piping arrangement was connected to an air manifold with three automated control

Fig. 4 Photobioreactor installed at East Bend Station

valves. When slurry pH rose above the desired set point (pH 7.0) the control valve connected to the flue gas would open, allowing flue gas to be introduced to the feed tank. When the pH dropped below the set point, the flue gas control valve would close and another control valve would open, allowing air in the head space to be recirculated, preventing CO_2 in the head space from venting from the system. The third control valve was used as a relief valve to prevent the feed tank from becoming pressurized as flue gas was added to the system. In this manner, as CO_2 was consumed by the algae, additional CO_2 was automatically fed into the system as needed to maintain the desired operating pH.

The PBR at East Bend Station was seeded on 7 December 2012 and operated continuously until 31 December 2012. During this time, flue gas was added as needed to maintain the pH at 7.0. Summary results (Fig. 6) show that productivity as high as 23 g/(m^2 day) was achieved during this period. These data also illustrate that productivity is related to available sunlight (i.e., PAR) as growth rate increased following periods of increased available PAR. The fact that the productivity data do not align perfectly with the PAR values requires comment, albeit that a clear trend is evident. This can be explained on the basis that (1) productivity is dependent on a combination of PAR and temperature (indeed, little growth was observed below 10 °C), and (2) the time at which the reactor is sampled during the day (am or pm) can introduce a lag into the data, i.e., samples taken in the early morning reflect growth the previous day (as well as night losses due to respiration), while samples taken in late afternoon reflect growth on the same day. During this time period, average daily temperature ranged from 4 to 20.5 °C. While this particular organism is not known to be particularly well suited for winter growth, reasonable growth rates were achieved, provided that sufficient PAR was available.

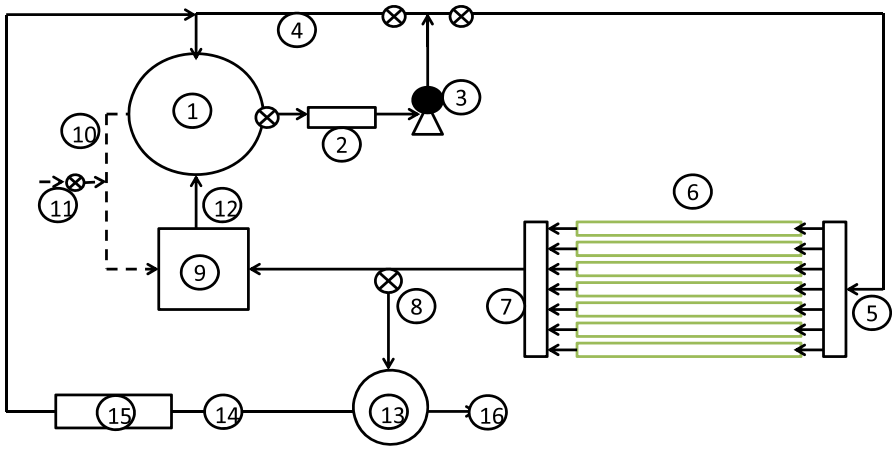

Fig. 5 Schematic of photobioreactor system at East Bend Station

1	Main Process Tank	9	Eduction / Gas Entrainment
2	Probe Housing	10	Head Space Circulation
3	Process Pump	11	CO_2 Addition
4	Bypass Loop	12	Process Return to Tank
5	Feed Manifold	13	Harvest Tank
6	Phototube Array	14	Supernate/ Nutrient Return
7	Return Manifold	15	UV Sterilization
8	Harvest Port	16	Concentrated Biomass Removal

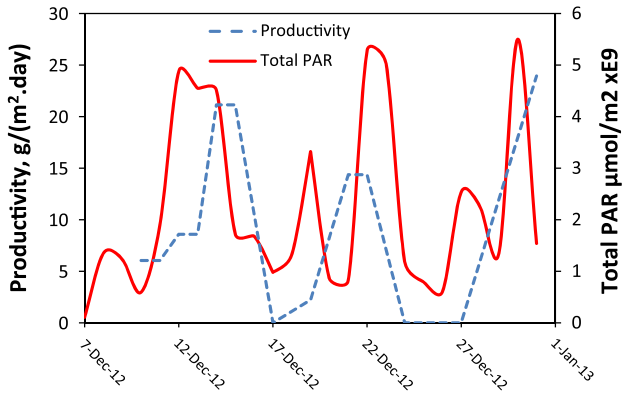

Fig. 6 Algal productivity and PAR during December growth study

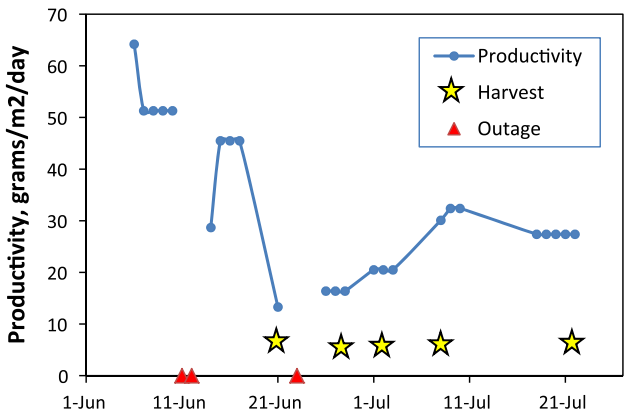

Fig. 7 Algal productivity during June–July growth study

Summer growth studies were conducted during June and July 2013 (see Fig. 7). As was observed with the winter growth study, productivity essentially followed periods of available sunlight (not shown). This study was complicated by several unforced electrical outages and an electrical failure to the feed system power supply caused by a lightning strike. Nevertheless, during periods of operation a mean growth rate of 32.9 g/(m^2 day) [with a standard deviation of 14.2 g/(m^2 day)] was recorded.

Harvesting and dewatering

During continuous PBR operation, it is necessary to periodically remove algae to control culture density to minimize self-shading and maintain culture health. Development of a suitable harvesting/dewatering strategy also addressed other system needs such as recycling clarified water to minimize water consumption and recycle unused soluble nutrients. Since the algae culture is very dilute (0.4–1.0 g dry mass/L), a cost effective, high capacity solid/liquid separation strategy was warranted. After considering a number of options, including dissolved air flotation and centrifugation, it was decided to pursue the use of sedimentation, thickening and filtration, an approach commonly used for treatment of industrial waste water.

Harvesting cycles were conducted as deemed necessary to maintain culture density, typically on a cycle of two to three times per week. A schematic diagram of the process is shown in Fig. 8. While the system continued normal

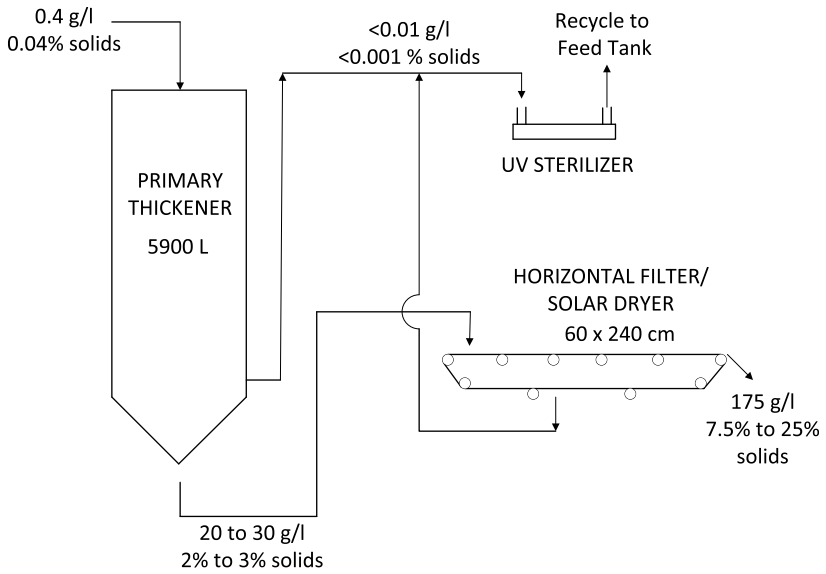

Fig. 8 Schematic diagram of harvesting/dewatering process

Table 3 Ultimate analyses of algal biomass harvested at East Bend Station (average of seven separate algae harvests ± standard deviation)

Carbon (%)	42.47 ± 4.18
Hydrogen (%)	6.50 ± 0.55
Nitrogen (%)	6.77 ± 0.70
Total sulfur (%)	0.52 ± 0.07
Oxygen (%)	24.38 ± 1.60
Ash (%)	19.36 ± 6.65
Volatile matter (%)	66.54 ± 4.25
Fixed carbon (%)	9.09 ± 2.40
As (ppm)	<0.1
Se (ppm)	<0.1
Cd (ppm)	<0.1
Hg (ppm)	<0.1

operation, approximately 4,000 L of culture was diverted into a cylindrical, cone bottomed harvesting tank. Moderate molecular weight cationic polyacrylamide flocculant was added at a dosage of 3–5 ppm, dependent upon harvest culture density, and mixed using a recirculating centrifugal pump. The flocculated system was allowed to settle for 4–8 h, after which settled biomass (20–30 g/L) was removed from the thickener and clarified water was pumped back into the feed tank to recycle water along with remaining soluble nutrients. As water was recycled, it was passed through a UV sterilizer. The concentrated algae slurry was then transferred to a horizontal gravity filter/solar dryer and allowed to drain on a multifilament filter fabric. Clear filtrate was passed through the UV sterilizer and returned to the feed tank and dewatered biomass cake was removed from the filter/dryer. If adequate sunlight was available, the filter cake was dry (≤3 % moisture) after approximately 24 h. If inadequate sunlight was available, the filter cake typically contained 7.5–25 % solids and was transferred to an oven and dried at 100 °C. After the biomass was thoroughly dried, a representative portion was characterized and the remainder stored in a freezer for utilization studies such as lipid extraction and upgrading.

Ultimate analyses of algal biomass harvested at East Bend are summarized in Table 3. The harvested biomass is characterized by an average of 42.47 % C and very high volatile matter content (66.54 %). Elemental analysis showed no detectable concentration of trace elements As, Se, Cd, and Hg within the detection limit of 0.1 ppm.

Upgrading of algal lipids to liquid fuels

Fatty acid methyl esters

To analyze the fatty acid profile of the lipids present in the harvested algae, lipids were extracted by the Bligh–Dyer method and converted to fatty acid methyl esters (FAME, more commonly referred to as biodiesel) via a sequence of esterification and transesterification. The gas chromatogram of the resulting FAME mixture is shown in Fig. 9 and the corresponding composition is summarized in Table 4. These results show that the oil consists mainly of C16:0 (palmitic), C18:1 (elaidic and oleic), C18:2 (linoleic) and C18:3 (linolenic) fatty acid chains. While C16 and C18 chain lengths are suitable for the production of diesel fuel hydrocarbons via hydrodeoxygenation or decarboxylation/decarbonylation (vide infra), or indeed for the production of biodiesel (FAME), higher value fatty acids such as EPA (eicosapentaenoic acid) and DHA (docosahexaenoic acid) are not present. Consequently, the value of the oil for nutraceutical purposes would be low.

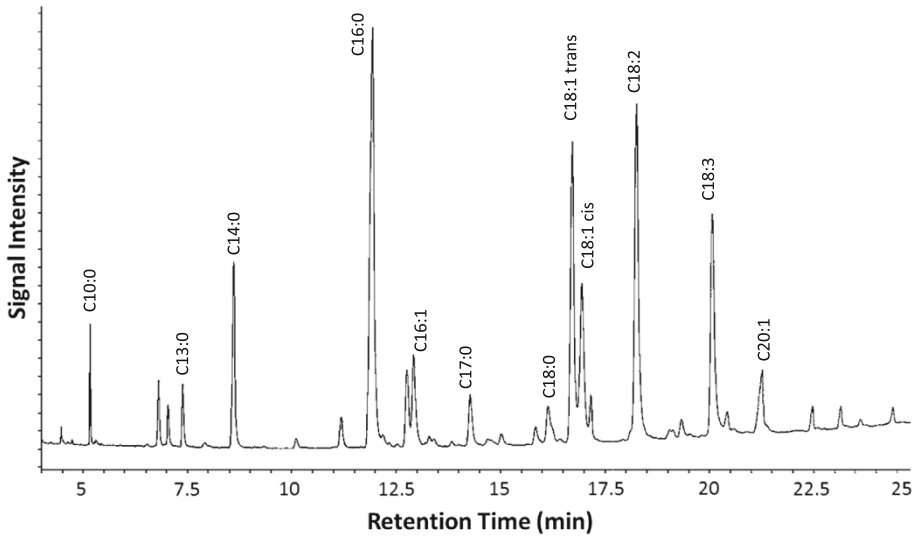

Fig. 9 Gas chromatogram of fatty acid methyl esters obtained from lipids extracted from *Scenedesmus acutus*

Table 4 Distribution of fatty acid chains in lipids extracted from *Scenedesmus acutus*

Fatty acid chain (*X*:*Y*)[a]	Algal lipid (GC area %)
Capric (10:0)	1.2
Tridecanoic (13:0)	1.3
Myristic (14:0)	5.3
Palmitic (16:0)	20.6
Palmitoleic (16:1)	3.9
Heptadecanoic (17:1)	2.0
Stearic (18:0)	2.1
Elaidic (18:1n9t)	12.1
Oleic (18:1n9c)	7.9
Linoleic (18:2)	15.3
γ-Linolenic (18:3n6)	10.5
Cis-11-eicosenoic (20:1)	3.3
Other	14.5

[a] *X*;*Y* = carbon number: number of double bonds

Diesel-range hydrocarbons

Hydrodeoxygenation (-H_2O) via hydrotreating forms the basis of a number of commercial or semi-commercial processes for the production of high quality drop-in hydrocarbon fuels from the lipids in vegetable oils and animal fats. Unfortunately, these processes require sulfided catalysts that risk contaminating the products with sulfur; in addition, they are constrained to use high pressures of H_2 that are typically only available in centralized facilities. An alternative lies in the deoxygenation of lipids via decarboxylation/decarbonylation ($deCO_x$), an approach that proceeds under considerably lower H_2 pressures and uses simple metal catalysts [24]. In recent work, we have shown that Ni-based catalysts are highly active for the upgrading of soybean oil and model triglycerides via $deCO_x$ [18, 19, 26]. Similarly, Lercher and co-workers have demonstrated that Ni-containing bifunctional catalysts can be employed to convert algal lipids to diesel-range alkanes in both batch and continuous modes (Peng et al. [22]; Peng et al. [23]; Zhao et al. [34].

Table 5 Conversion of algae oil to diesel-range hydrocarbons

Catalyst	Conversion	Selectivity to C10–C17 (%)[a]	Selectivity to C17 (%)
Ni–Al LDH	95	73	7

Conditions: fixed bed reactor, 300 °C, 580 psi H_2, feed = 1.33 wt% algae oil in dodecane, feed rate = 6 mL/h

[a] Note that this value underestimates actual C10–C17 selectivity due to the fact that any C12 produced is not included in the calculation (given that C12 is used as the reaction solvent)

Building on the above studies, oil extracted from *Scenedesmus* microalgae harvested from the East Bend facility was subjected to upgrading via catalytic decarboxylation/decarbonylation. Prior to upgrading, the crude lipids were purified by filtration through K10 montmorillonite (an acid-treated clay) to remove chlorophyll (the presence of which might lead to the formation of deposits such as coke and Mg^{2+} on the catalyst during reaction). The purified oil was then upgraded as a solution in dodecane over a Ni/Al layered double hydroxide (LDH) catalyst [25] in fixed bed mode under H_2 (580 psi). Results are summarized in Table 5 and Figs. 10 and 11.

These results confirm that catalytic $deCO_x$ is a viable process for the conversion of microalgal lipids to diesel/jet fuel range hydrocarbons. Notably, some C18 is obtained (with 5 % selectivity), indicating that hydrodeoxygenation occurs in parallel with decarbonylation/decarboxylation, although together the latter processes constitute the major pathway given the higher selectivity of C17 observed. It is

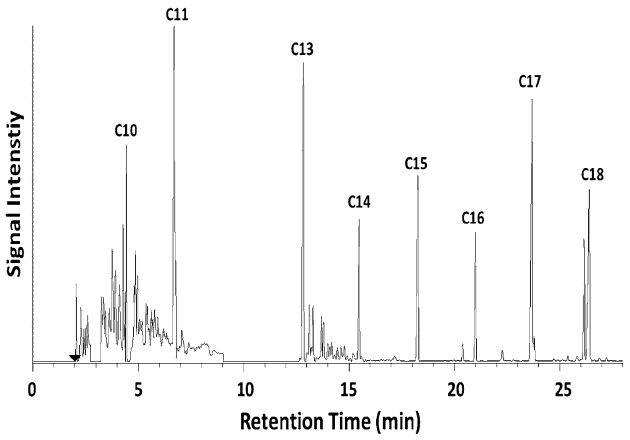

Fig. 10 Gas chromatogram of liquid product sampled after 4 h on stream during decarbonylation/decarboxylation of algal lipids. Note that the dodecane solvent (C12) has been subtracted from the chromatogram

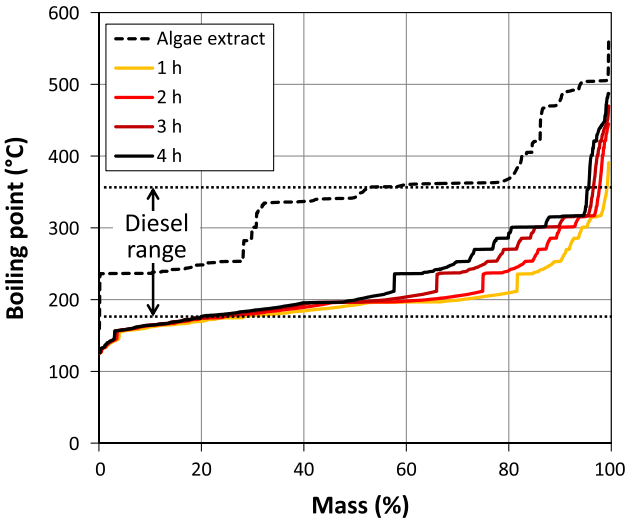

Fig. 11 Simulated-distillation boiling point distribution plots of algal lipid feed and liquid product sampled at 1, 2, 3, and 4 h during decarboxylation/decarbonylation. Note that the dodecane solvent (C12) has been removed from the plots

also evident that cracking of the unsaturated C18 fatty acid chains occurs, given the significant amounts of C10–C13 hydrocarbons obtained. Such cracking may or may not be beneficial depending on whether hydrocarbons are being targeted for jet fuel/lighter diesel-range applications or not. In other work [18, 19], we have found that less highly unsaturated fatty acid chains produce comparatively higher yields of the longer chain hydrocarbons (e.g., C15 and C17), which are well suited for diesel fuel blending.

Preliminary techno-economic analysis

The baseline scenario considered for this study was a 1,000 MW power plant, requiring 30 % CO_2 capture. Key inputs and assumptions used are collected in Table 6, while Table 7 summarizes the calculated costs associated with CO_2 capture. The techno-economic model is based on the capital and operating costs of a microalgae cultivation system sized to consume a given amount of CO_2. On a stoichiometric basis, algae consume ~1.76 tons of CO_2 to produce 1 ton of algal biomass, the exact figure depending on the elemental composition of the biomass produced [1]. The CO_2 emissions are based on the average rating of a coal-burning power plant, which relates the BTU content of the coal to the CO_2 emission. Algal productivity is expressed in grams per meters squared per day, a value of 30 g/(m^2 day) being used in this analysis. This number is derived from East Bend Station data (collected in the months of December, June and July) and data collected at the University of Kentucky (UK) over an approximately 12 month period; the East Bend data followed the trends previously observed at UK with respect to algae productivity as a function of the time of year. Relating algal

Table 6 Summary of inputs and assumptions used in the techno-economic analysis (base case)

Input	Value	Comment
Required CO_2 capture efficiency	30 %	Required capture efficiency if CO_2 emissions are to be maintained at 1,990 value
PBR cost, $/L (raw materials)	0.55	Custom design, PETG and PVC parts. Current cost, discounted by 55 % for bulk manufacture of parts
PBR installation cost, $/L	100	Assumed to be 100 % of raw material costs
PBR tube useful life, years	5	UV degradation limits tube life
Operation and maintenance costs, $/L	5 %	Labor + minor consumables, 5 % of PBR material costs
Areal productivity, g/(m^2 day) (year average)	30	Value based on data collected at East Bend Station and at the University of Kentucky
Nutrient costs, $/kg algae	0.14	Nutrient recipe utilizes bulk grade fertilizer
Nutrient recycle	97 %	Water + nutrients from algae harvesting and dewatering are recycled
Flocculant concentration, ppm	3	Commercial cationic flocculant
Flocculant cost, $/kg	4.40	Commercial cationic flocculant
Electricity cost, $/kWh	0.02	Discounted rate at utility site
Water cost, $/L	–	Water at site is free
Operating days per year	300	Estimated power plant operation (allowing for plant maintenance and unscheduled outages)
Payback period, years	10	Assumed payback time

Table 7 Summary of costs associated with CO_2 mitigation using microalgae

	Cost in $ per ton of CO_2 removed
Growing system	
PBR capital	775
PBR installation	775
PBR operation and maintenance	40
Energy	1
Nutrients	15
Growth subtotal	1,606
Dewatering	
1st stage dewatering	15
2nd stage dewatering	0.50
Dewatering subtotal	15.50
Total cost	1,621

productivity to the carbon emissions of a typical coal-fired power plant results in the total land area required for the cultivation system, i.e., an algae farm big enough to consume the requisite amount of CO_2. Based on this productivity, a cultivation system equivalent to 26,200 acres (40.9 square miles) would be required for the baseline scenario (30 % CO_2 mitigation for a 1,000 MW capacity plant). The costs associated with this process (capital, operating, dewatering) are then normalized by land area ($/m^2) to be compared with areal productivity, and thereby CO_2 consumption. As with capital costs, the energy consumption of the PBR system is extrapolated from current system values. The pressure drop associated with adding additional tubes in series is negligible, resulting in a lower energy cost per unit area (Watts/m^2) of installed and operating PBR. [Note that each tube pair has a calculated pressure drop of 0.00134 psi based on the frictional resistance; a module of 500 tubes as for the East Bend PBR has 25 tube pairs (10 rows) and would, therefore, have a pressure drop of 0.034 psi]. In this way, we are able to estimate the costs associated with consuming a ton of CO_2.

The key assumptions start with the size of the power plant, combined with the percentage of flue gas to be consumed, which together set the CO_2 emission rate of the system. In this case, we based our system on a 300 MW slip stream from a 1 GW plant, i.e., a 30 % slipstream. Operating days per year (300) and an amortization period are chosen to calculate the total amount of CO_2 that would be emitted over the lifetime of the algae-based mitigation system. The overall capital costs are estimated based on the current design of the demonstration facility at East Bend Station and are normalized based on the land area that the system would occupy. The most important assumption is areal productivity, which controls the size and thereby cost of the overall system.

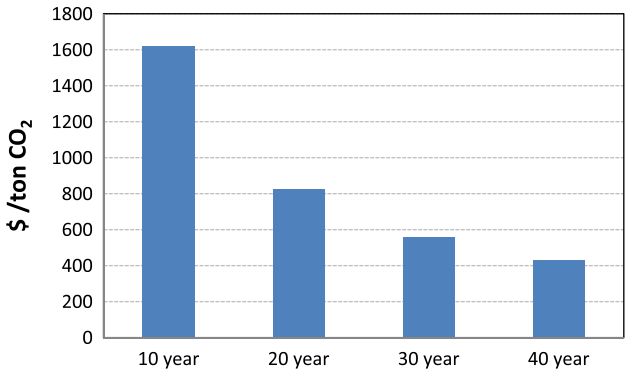

Fig. 12 Effect of amortization period on the cost of CO_2 capture

Although significant progress was made in reducing both the capital and recurring operating costs of the PBR employed, according to the analysis in Table 7, the current cost of capturing CO_2 falls close to $1,600/ton. Moreover, the capital cost and installation of the algae growth facility constitute 98 % of the overall cost of CO_2 capture. Further progress is clearly needed to reduce the overall capital cost of the system and thus reduce the cost of CO_2 capture. In addition, it should be noted that an amortization period of 10 years was used in the analysis. A less conservative approach would involve increasing this 10 year period to longer periods, bearing in mind that the contribution of operations and maintenance should be increased accordingly. Specifically, allowance has to be made for replacement of the PET tubes every 5 years, these comprising 8 % of the total capital cost; other parts are fabricated from PVC and are assumed to have a lifetime of >30 years. As shown in Fig. 12, extending the operating life of the facility improves the cost per ton of CO_2 mitigated considerably, although further cost reductions would require a decrease in the various cost elements associated with the PBR. A second option would be to increase the areal productivity although the scope for this seems limited given climatic constraints.

An important consideration is that this analysis takes no account of the value of the algal biomass produced. From this, it follows that there is a strong incentive to maximize this value, e.g., by conversion of the biomass to valuable products (nutraceuticals, animal food additive, premium organic fertilizer, etc.), to generate a revenue stream which can help to defray the costs of CO_2 capture/recycle. The size of the markets for algae-derived products is inversely related to the product price. Lower value products such as liquid fuels may be less attractive from a profitability perspective, but a utility-scale installation would produce a quantity of algal biomass that would inevitably oversupply lower volume, higher value product markets. However, there is no reason that utility-scale biomass utilization could not focus on developing both markets; lower value markets to utilize significant volumes, along with limited

participation in higher value markets to maximize profits. By doing so, higher value market supply, and hence, profitability will be maintained.

Conclusions

Based on our initial work, we conclude that CO_2 capture and recycle using microalgae is feasible from a technical standpoint. By applying PBR technology, that was developed in-house, at East Bend Station, Kentucky, and using flue gas as the CO_2 source, algae productivity of routinely $\geq$30 g/(m^2 day) in the summer months was achieved at significant scale (18,000 L). These values compare favorably with values reported in the literature for both pond- and PBR-based cultivation studies. Moreover, average daily productivity slightly in excess of 10 g/(m^2 day) was demonstrated in the month of December and 39 g/(m^2 day) in June–July. To harvest and dewater the produced algal biomass, a protocol was developed based on flocculation and sedimentation, followed by filtration. Extraction of lipids from the harvested biomass was also demonstrated, followed by their conversion to diesel-range hydrocarbons via catalytic deoxygenation.

Conservative estimates suggest that the current cost of capturing and recycling CO_2 using this approach will fall close to \$1,600/ton CO_2 (assuming an amortization period of 10 years). The largest sources of cost reside in the algae culturing stage of the process, corresponding mainly to the capital cost of the photobioreactor system and the associated installation cost. From this it follows that future cost reduction measures should focus on the design of a culturing system which is less expensive to build and install. Even in the most optimistic scenario, the cost of algae-based CO_2 capture is unlikely to fall below \$225/ton, corresponding to a production cost of $\sim$\$400/ton biomass. Clearly, the economics of CO_2 capture and recycle can be significantly improved if the algal biomass produced can be sold. In view of the fact that the markets for algae are in their infancy, the value of algal biomass is at present hard to quantify with the exception of its fuel value. That said, the literature suggests that several large-volume markets do exist, such as animal feed and organic fertilizer, albeit that these applications require the absence of bioaccumulated heavy metals in the biomass. In this regard, the absence of heavy metals in the algae grown at East Bend, at a detection level of 0.1 ppm, is encouraging.

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